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Inductively Coupled Plasma-Atomic Emission Spectrometric Analysis of Environmental Samples Using Ultrasonic Nebulization

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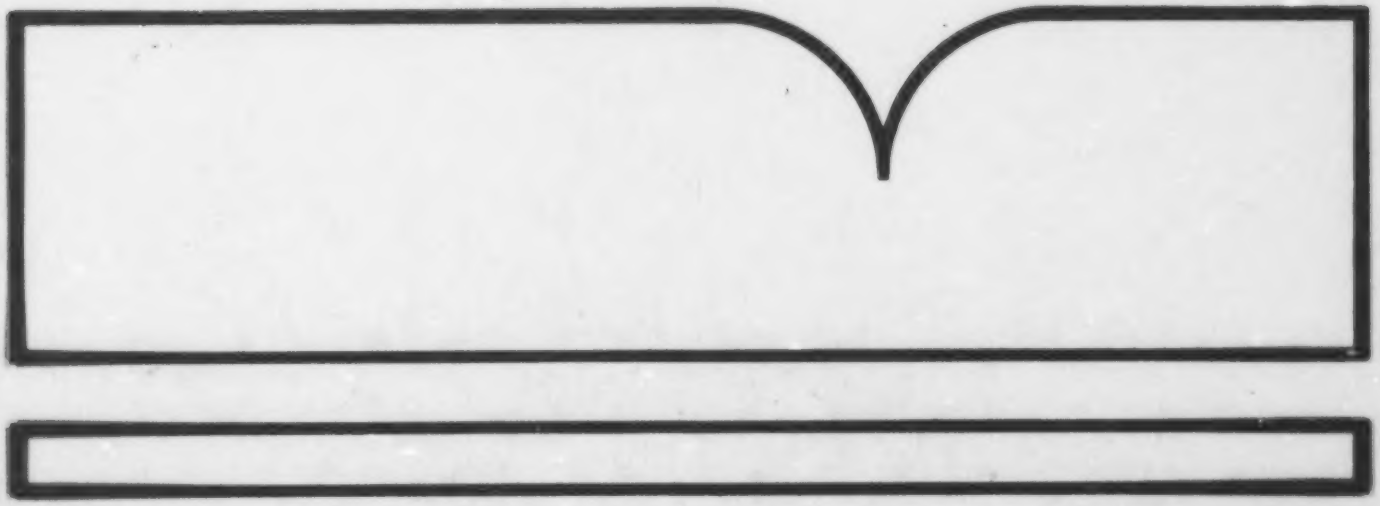

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16. ABSTRACT

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Inductively Coupled Plasma-Atomic Emission Spectrometric Analysis of Environmental Samples Using Ultrasonic Nebulization

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Ultrasonic and pneumatic nebulizers used in inductively coupled plasma-atomic emission spectrometry (ICP-AES) are compared in the analysis of standard materials and environmental samples. Results verify that ICP-AES with ultrasonic nebulization is capable of lower detection limits than ICP-AES with a pneumatic system. The ultrasonic system used with desolvation, therefore, is the more desirable system when ultratrace ICP-AES quantitative analyses are required in a variety of environmental samples.

Index Headings: **Emission spectroscopy; Inductively coupled plasma; Elemental analysis; Ultrasonic nebulization.**

INTRODUCTION

Extensive applications of inductively coupled plasma-atomic emission spectrometry (ICP-AES) using different types and designs of sample introduction systems have been described.[1] Most standard equipment nebulizers on today's commercially available instruments are assorted designs of the pneumatic type. Different pneumatic nebulizers can be chosen by users to satisfy their individual analytical requirements. Since only slight differences in detection limits have been reported by investigators using various types of pneumatic nebulizers,[2] the selection of a particular pneumatic nebulizer is usually based on some criteria other than detection limits. Considerations might include long- and short-term stability, analysis precision, fragility, susceptibility to blockage, and memory effects.

Although detection limit capabilities of ICP-AES with a pneumatic nebulizer are adequate for many applications, some analytical requirements are outside its quantitative range. For example, compliance with the U.S. Environmental Protection Agency's Primary Maximum Contaminant Levels for Inorganic Chemicals in Drinking Water[5] cannot be established using the pneumatic nebulizer system.

To meet the requirements of the primary drinking water contaminants analysis, the ultrasonic nebulizer has been used with the ICP-AES.[1] This combination offers

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the desirable features of high sample throughout, wide dynamic range of operation, acceptable precision and accuracy, and simultaneous quantitative analytical capabilities for all elements except mercury in these drinking water requirements. Moreover, the ultrasonic nebulizer does not require sample preconcentration, a procedure in the preparation of samples that can introduce contamination. This paper compares the ultrasonic nebulizer with a pneumatic nebulizer using standard materials and environmental samples to demonstrate respective capabilities for ultratrace ICP-AES quantitative analyses.

I. EXPERIMENTAL

A. Instrumentation. The ICP-AES instrument used in this study is an ICP-QA 137 (Applied Research Laboratories, Sunland, CA). The most significant change made to the instrument was replacement of the mechanically ruled 1920 grooves/mm grating with a holographically recorded 1920 grooves/mm grating, which was described in an earlier paper.[3] The spectrometer line array shown in Table I indicates lines for which solar blind photomultipler tubes (Hamamatsu, Middlesex, NJ) have been installed.

The concentric design, pneumatic nebulizer (model no. TR-20-AL, Meinhard Associates, Tustin, CA) used in this study was included with the original equipment delivered with the ICP-AES. The computer controlled desalter and the argon humidifier were not being used at the time of this experiment. The aerosol chamber was the dual tube type that also was standard equipment.

The commercially available ultrasonic nebulizer system (Plasma-Therm, Inc., Kresson, NJ) consisted of an rf power supply, a nebulizer chamber with an ultrasonic transducer, and a peristaltic metering pump. The condenser used for the system is the bulb type Allihn (Fisher Scientific, Pittsburgh, PA) modified with ball joint connectors at the inlet and outlet. Various desolvator column designs were tested, but results were not significantly different from the data shown in Table II. The desolvator shown in Fig. 1 was fabricated locally following a design originally used at the Department of Energy, Ames Laboratory, Iowa State University. Some changes (shown in Fig. 2) were made in the configuration of the nebulizer chamber that houses the ultrasonic transducer. The glass nebulizer chamber was modified to facilitate operation of the transducer in the vertical rather than the horizontal position. These modifications allowed production of the desired sample mist with a reduced rf power supply setting. Another useful change to the ultrasonic nebulizer

TABLE I. Spectrometer line array.

Element[a]	Wavelength (Å)[b]	Element[a]	Wavelength (Å)[b]
Ag I	3280.7	Mo II X	2871.5
Al I	3082.2	Na I	3302.3
As I X	1937.6	Ni II X	2316.0
B I X	2496.8	Pb II X	2203.5
Ba II	4554.0	Sb I X	2068.4
Be II	3130.4	Se I X	1960.9
Bi I X	2230.6x2	Sn I	3034.1
Ca II	3158.9	Sr II	4077.7
Cd II X	2265.0	Te I X	2142.8x2
Co II X	2286.2x2	Th II	4019.1
Cr II X	2677.2	Ti II	3685.2
Cu I	3247.5	Tl I	3519.2
Fe II X	2599.4	V II X	2924.0
Hg I X	2536.5	Y II	3710.3
Mg II	2790.8	Zn I X	2138.6
Mn II X	2576.1		

[a] I denotes radiation originating from neutral atom; II denotes radiation originating from singly ionized atoms; X denotes solar blind photomultiplier tube detector.

[b] All line orders are noted if different than first order; x2 is for second order lines.

TABLE II. ICP-AES detection limits.

Element (Å)		Detection limit (mg/liter)[a]	
		Pneumatic	Ultrasonic
Ag	3280.7	0.005	0.0008
Al	3082.1	0.04	0.003
As	1937.6	0.06	0.006
B	2496.8	0.009	0.004
Ba	4554.0	0.0003	0.00009
Be	3130.4	0.0002	0.00004
Bi	2230.6	0.05	0.009
Ca	3158.9	0.006	0.002
Cd	2265.0	0.005	0.0003
Co	2286.2	0.006	0.0004
Cr	2677.2	0.005	0.0003
Cu	3247.5	0.003	0.0008
Fe	2599.4	0.002	0.0002
Hg	2536.5	0.015	0.004
Mg	2790.8	0.03	0.003
Mn	2576.1	0.00045	0.00008
Mo	2871.5	0.012	0.002
Na	3302.3	1.5	0.24
Ni	2316.0	0.03	0.0010
Pb	2203.5	0.03	0.002
Sb	2068.4	0.05	0.004
Se	1960.9	0.6	0.003
Sn	3034.1	0.06	0.004
Sr	4077.7	0.00006	0.00003
Te	2142.8	0.05	0.0010
Th	4019.1	0.012	0.0013
Ti	3519.2	0.002	0.0002
Tl	3519.2	0.075	0.02
V	2924.0	0.002	0.0003
Y	3710.3	0.0008	0.00008
Zn	2138.6	0.008	0.0008

[a] Detection limit is three times the standard deviation of background emission.

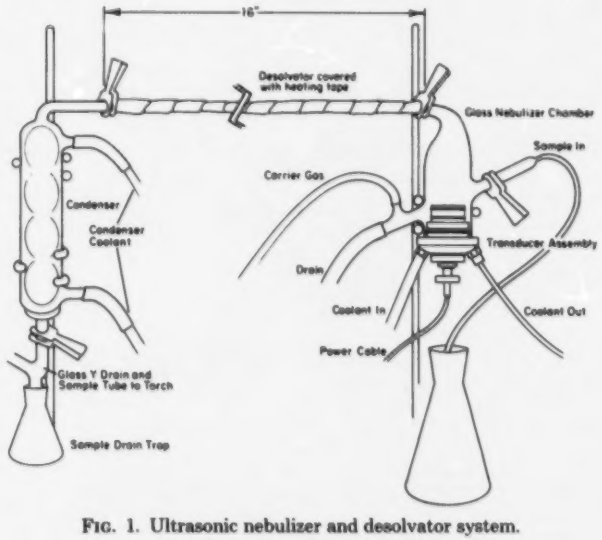

FIG. 1. Ultrasonic nebulizer and desolvator system.

system was enlargement of one of the cooling water lines to the Teflon portion of the transducer mounting assembly. Using an enlarged cooling connector as the inlet side for the cooling water assures a more positive supply of water for sufficient transducer cooling and also helps to eliminate formation of air pockets in the system.

B. Operating Conditions. The ICP-AES source was operated at rf forward power of 1.6 and 2.0 kW, respectively, for the pneumatic and ultrasonic nebulizer systems. Argon flow rates for plasma, auxiliary, and carrier gases were 16, 1.6, and 1 liters/min, respectively, for the pneumatic nebulizer system and were increased to the values of 18, 1.6, and 1 liters/min with the ultrasonic nebulizer system. Observation heights were 17 mm above the load coil with the pneumatic system and 19 mm for the ultrasonic system. The operating conditions chosen were found to be optimum for compromise simultaneous multielement analysis when using the particular nebulizer under study. The standard ICPQuantometer-BLISS system described previously by Dahlquist and Knoll[4] was used for data acquisition and processing.

C. Reagents and Materials. Distilled-deionized water was used in sample and standard preparations. Standard reference solutions were purchased from two vendors (Spex Industries, Inc., Metuchen, NJ; National Spectrographic Laboratories, Inc., Cleveland, OH). Nitric acid used in calibration standards and other solutions was Ultrex (J. T. Baker, Phillipsburg, NJ).

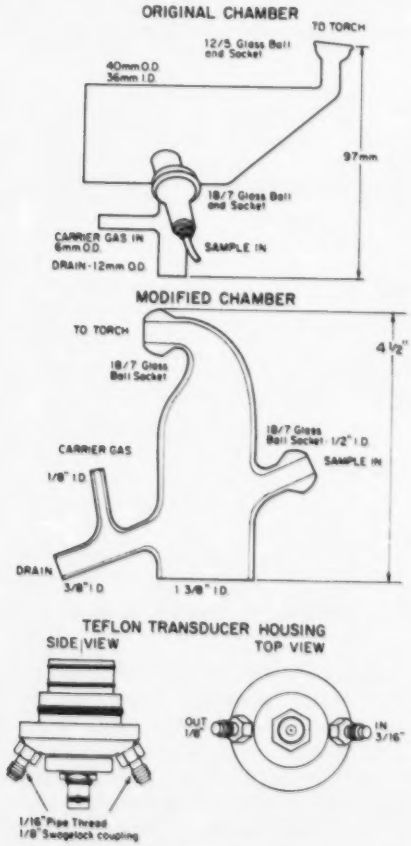

FIG. 2. Original and modified transducer chambers.

II. RESULTS AND DISCUSSION

A. Detection Limits. The detection limit (three times the standard deviation of background emission) data for 31 elements obtained using pneumatic and ultrasonic nebulizer systems are summarized in Table II. Both sets of data were determined from single element standards in 1% nitric acid solutions. Eleven 10-s integrations were used for the calculation of each detection limit for both the pneumatic and ultrasonic nebulizers. These data show a gain in detection limits by factors of 5 to 10 and in some cases (such as lead and nickel) greater than 10.

B. Maximum Contaminant Levels for Inorganic Chemicals in Community Water Systems. Maximum contaminant levels for inorganic chemicals in drinking waters[5] are shown in Table III along with detection limit data for both the pneumatic and ultrasonic nebulizer systems. The lowest quantitative determinable concentration (10 times the standard deviation of background emission) values shown in Table III indicate that the pneumatic nebulizer system fails to meet quantitative drinking water requirements for five (As, Cd, Pb, Hg, and Se) of the eight elements. Whereas with ultrasonic nebulization only Hg has a lowest quantitative determinable concentration value higher than the maximum permissible contaminant level.

C. Analysis of Drinking Water. Drinking waters have been analyzed using the ultrasonic and pneumatic nebulizer systems; a typical comparison is shown in Table IV. In analysis of such samples where concentrations allow comparison of data acquired with pneumatic and ultrasonic nebulizer systems, the two systems show good agreement (Table IV). The major differences in the two nebulizer systems to be noted from these data are the lowest quantitative determinable values that can be stated for each system. Rinse times between samples for both nebulizer systems were found to be the same for the sample types analyzed in these studies.

D. Analysis of Municipal Sewage Influent and Effluent Waters. Intensity measurements were made as the wavelength region adjacent to the analytical line was scanned by stepping the primary slit along the Rowland circle. These wavelength profiles were obtained for

TABLE III. Maximum contaminant levels for inorganic chemicals in drinking water and ICP detection limit data.

Contaminant	Maximum level (mg/liter)	ICP Nebulizer			
		Pneumatic		Ultrasonic	
		DL[a] (mg/liter)	LQD[b] (mg/liter)	DL[a] (mg/liter)	LQD[b] (mg/liter)
Arsenic	0.05	0.06	0.210[c]	0.006	0.020
Barium	1	0.003	0.009	0.00009	0.0003
Cadmium	0.010	0.005	0.015[c]	0.0003	0.001
Chromium	0.05	0.005	0.015	0.0003	0.001
Lead	0.05	0.030	0.100[c]	0.002	0.005
Mercury	0.002	0.015	0.050[c]	0.004	0.015[c]
Selenium	0.01	0.060	0.300[c]	0.003	0.010
Silver	0.05	0.005	0.025	0.0008	0.0025

[a] Detection limit (DL) is three times the standard deviation of background emission.

[b] Lowest quantitative determinable concentration (LQD) is 10 times the standard deviation of background emission.

[c] Underscored values indicate LQD exceeds maximum contaminant level concentration.

pneumatic and ultrasonic nebulization of the solution. Representative of these scan data are Figs. 3 and 4, which show the analyte signals of cadmium 2265.0 Å and cobalt 2286.2 Å, respectively. The round robin municipal sewage samples had been spiked with 0.105 ppm Cd and 0.120 ppm Co.

Figs. 3 and 4 show that there is essentially no change in background structure between the blank and sample, nor between pneumatically and ultrasonically nebulized solutions. The slightly higher overall background observed with the ultrasonically nebulized solution can be attributed to the higher (2 kW) power used. When net line intensities are compared, an approximate 13-fold increase for Cd and an approximate 15-fold increase for Co are observed when ultrasonic nebulization is employed. These enhanced line-to-background signals are clearly demonstrated in Figs. 3 and 4, where the analyte signal for pneumatic nebulization is barely distinguishable from the background signal. The results obtained by this laboratory and other laboratories participating in the round robin study are summarized in Table V.

Table VI presents a comparison of the results obtained with ICP-AES (pneumatic), flame atomic absorption, and ICP-AES (ultrasonic) in the analysis of Pb in sewage samples. The sample labeled "Effluent" contained only the Pb present in the sewage, while the "Influent" sample had been spiked with 0.060 ppm Pb by the issuing laboratory in a round robin study.

The data show that where elemental concentrations allow comparison, results of all methods show good agreement. When lower concentrations of Pb (~0.03 and ~0.09 ppm) were sought, however, ICP-AES with ultrasonic nebulization provided quantitative information whereas the other methods could only supply "less than" values. Although no rigorous statistical evaluation was attempted, the two (separate) determinations using ultrasonic nebulization show good reproducibility and the calculated recovery ("Influent" minus "Effluent") of

TABLE IV. Analysis of drinking water.

Element	Conc (mg/liter)[a] ICP ultrasonic	Conc (mg/liter)[a] ICP pneumatic	Element	Conc (mg/liter)[a] ICP ultrasonic	Conc (mg/liter)[a] ICP pneumatic
Ag	<0.003	<0.025	Mo	<0.007	<0.040
Al	0.034	0.038	Na	1.61	<5
As	<0.020	<0.21	Ni	<0.003	<0.10
B	<0.013	<0.030	Pb	<0.007	<0.10
Ba	0.002	0.001	Sb	<0.013	<0.17
Be	<0.0001	<0.0004	Se	<0.010	<0.30
Bi	<0.030	<0.17	Sn	<0.013	<0.17
Ca	19.0	19.1	Sr	0.074	0.071
Cd	<0.001	<0.015	Te	<0.030	<0.17
Co	<0.001	<0.020	Th	<0.004	<0.04
Cr	<0.001	<0.015	Ti	<0.0007	<0.007
Cu	<0.003	<0.010	Tl	<0.060	<0.25
Fe	0.045	0.041	V	<0.001	<0.007
Hg	<0.015	<0.05	Y	<0.0003	<0.003
Mg	0.701	0.715	Zn	<0.002	<0.02
Mn	0.001	<0.002			

[a] < values are calculated lowest quantitative determinable concentration (10 times the standard deviation of background emission).

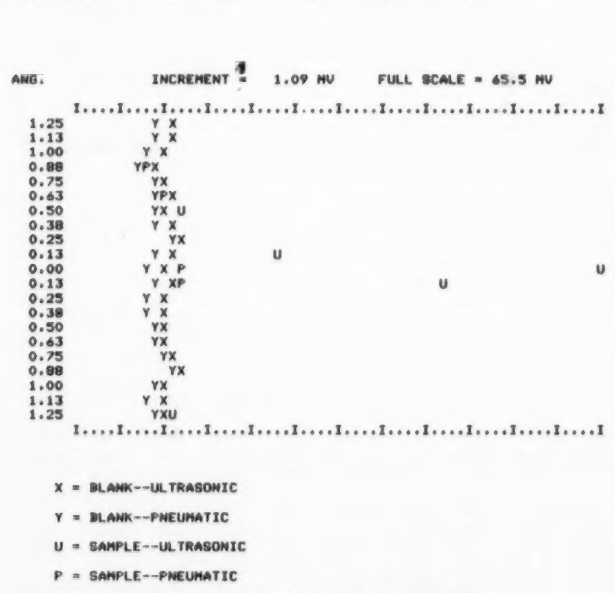
ULTRASONIC VS. PNEUMATIC -- SEWAGE SAMPLES CD 2265
ANG. INCREMENT = 1.09 MV FULL SCALE = 65.5 MV
X = BLANK--ULTRASONIC
Y = BLANK--PNEUMATIC
U = SAMPLE--ULTRASONIC
P = SAMPLE--PNEUMATIC

FIG. 3. Wavelength scan at Cd 2265.0 Å.

ULTRASONIC VS. PNEUMATIC -- SEWAGE SAMPLES CO 2286.2
ANG. INCREMENT = 1.23 MV FULL SCALE = 73.5 MV
X = BLANK--ULTRASONIC
Y = BLANK--PNEUMATIC
U = SAMPLE--ULTRASONIC
P = SAMPLE--PNEUMATIC

FIG. 4. Wavelength scan at Co 2286.2 Å (second order).

TABLE V. Analysis of municipal sewage.[a]

	Conc (mg/liter) Mean of 4[b] pneumatic ICAP	Mean of 4 flame AA	Range pneumatic ICAP	Range flame AA	Ultrasonic ICAP[b]
Ca	21.6	23.0	19.2–22.8	20.1–28.0	21.9
Mg	22.0	22.0	22.2–23.5	20.5–24.0	20.0
Al	0.56	0.64	0.44–0.69	0.60–0.78	0.50
Cd	0.091	0.093	0.056–0.100	0.07–0.110	0.105
Co	0.108	0.100	0.05–0.133	0.065–0.140	0.122
Cr	0.303	0.328	0.300–0.308	0.310–0.340	0.330
Ni	0.094	0.093	0.070–0.136	0.086–0.100	0.102

[a] All data except ultrasonic inductively coupled argon plasma (ICAP) are from round robin study. AA, atomic fluorescence.
[b] Sample preparation Ref. 14.

0.056 ppm Pb agrees well with the amount actually added (0.060 ppm Pb).

The data presented in Table VII are the results of the analysis of one representative municipal sewage sample from a set of six analyzed in this study. The samples were digested in accordance with the proposed EPA-ICP method,[6] which is a HNO_3-HCl digestion procedure. The aliquot used for a set A was filtered as specified in the proposed method,[6] whereas the set B aliquot was not filtered but was agitated during sample injection into the ultrasonic nebulizer.

The decreases in concentration between set A and set B in Table VII occurred with all six samples. Lower concentrations in the filtered samples for the elements Al, As, Ca, Cu, Fe, Hg, Na, Se, Ti, and Zn are assumed to be due to the loss of analyte as particulate in the filtration or the loss of analyte by adsorption of the ion on the filtering medium, or to a combination of the two mechanisms.

As is noted in this procedure[6] and elsewhere,[7] undissolved material in some wastewaters may plug the small orifices of concentric and cross flow pneumatic nebulizers. Our experience has been that plugging by solids is not a problem when using the ultrasonic nebulizer system.

Since the optimum carrier flow rate for sample introduction into the ICP is rather low (on the order of 1 liter/min of aerosol carrier gas) very small orifices are required with most pneumatic aerosol generation techniques. The use of larger orifices with these conventional pneumatic nebulizers would require that one either operate the carrier flows higher than is optimal for simultaneous multielement analysis or employ some technique[8] such as stream splitting to keep the aerosol injection rate low. The ultrasonic nebulizer, however, is well suited for operating at these low carrier gas flow rates since nebulization is accomplished with a vibrating transducer rather than by the shearing force by a high velocity gas stream across the liquid surface. The result is that the sample can be injected into the plasma at the required rate while an essentially nonrestrictive path for sample transport is still maintained, thus alleviating the problem of orifice plugging.

E. Effect of Organic Acids and Moderately High Salt Concentration on the Ultrasonic Nebulizer. To examine the effects of organic acids and salt on ICP-AES using the ultrasonic system, a series of samples were analyzed for all metal priority pollutants except Hg; results are shown in Table VIII. Duplicate samples were prepared for each set; O set contained no organic acids, H set contained humic acids, F set contained fulvic acids, and M set contained a mixture of humic and fulvic acids.

TABLE VI. Analysis of trace amounts of lead in sewage samples.

Lead conc (mg/liter) in sample run					
ICAP pneumatic		Atomic absorption		ICAP ultrasonic[b]	
Effluent (not spiked)					
Lab 1	<0.200	Lab 5	<0.05	0.033	(Two separate
2	0.016	6	<0.02	0.030	preparations and
3	0.074	7	<0.05		determinations)
4	<0.05	8	<0.100		
Influent (spiked with 0.06 mg/liter)					
Lab 1	<0.200	Lab 5	0.100	0.092	(Two separate
2	0.096	6	0.070	0.085	preparations and
3	0.142	7	<0.05		determinations)
4	0.067	8	<0.100		

[a] Determination by ultrasonic inductively coupled argon plasma (ICAP) at this laboratory.

TABLE VII. Analysis of filtered and unfiltered digested sewage samples.

Element	Conc (mg/liter) Set A filtered ICP	Set B unfiltered ICP	Element	Conc (mg/liter) Set A filtered ICP	Set B unfiltered ICP
Ag	0.023	0.026	Mo	<0.006	<0.006
Al	0.406	0.931	Na	1.20×10^2	1.63×10^2
As	0.046	0.072	Ni	<0.002	0.006
B[a]	1.10	1.31	Pb	0.029	0.030
Ba	0.087	0.105	Sb	<0.005	0.071
Be[b]	<0.0001	<0.0001	Se	0.025	0.034
Bi	<0.030	0.030	Sn	<0.013	<0.013
Ca	1.15×10^1	1.38×10^1	Sr	0.076	0.090
Cd	0.002	<0.001	Te	<0.033	<0.033
Co	0.002	<0.001	Th	<0.005	<0.005
Cr	0.100	0.114	Ti	<0.001	0.046
Cu	0.090	0.204	Tl	<0.06	<0.06
Fe	0.595	0.828	V	0.001	<0.001
Hg	0.084	0.093	Y	<0.0002	<0.0002
Mg	2.55	2.52×10^1	Zn	0.056	0.073
Mn	0.078	0.090			

[a] Samples prepared in glass.
[b] All values preceded by (<) are lowest quantitative determinable concentration estimates for the element.

TABLE VIII. Analyses of solutions containing salt and organic acids.[a]

	As	Ag	Cd	Cr	Cu	Co	Fe	Mn	Ni	Pb	Se	Tl	Zn
Duplicates, no organic acids													
I/O	0.165	0.162	0.174	0.177	0.189	0.200	0.171	0.178	0.171	0.178	0.165	0.160	0.175
2/O	0.171	0.158	0.176	0.177	0.188	0.199	0.171	0.178	0.171	0.180	0.170	0.157	0.172
Mean	0.168	0.160	0.175	0.177	0.189	0.200	0.171	0.178	0.171	0.179	0.168	0.159	0.174
Duplicates, 9 ppm by weight, humic acid													
I/H	0.163	0.160	0.172	0.175	0.190	0.198	0.175	0.177	0.170	0.176	0.171	0.158	0.175
2/H	0.158	0.162	0.172	0.175	0.190	0.201	0.177	0.178	0.169	0.171	0.172	0.160	0.172
Mean	0.161	0.161	0.172	0.175	0.190	0.200	0.176	0.178	0.170	0.174	0.172	0.159	0.174
Duplicates, 5 ppm by weight, fulvic acid													
I/F	0.164	0.164	0.173	0.176	0.192	0.206	0.178	0.175	0.173	0.180	0.178	0.161	0.176
2/F	0.163	0.166	0.178	0.172	0.189	0.204	0.174	0.173	0.175	0.178	0.176	0.167	0.176
Mean	0.164	0.165	0.176	0.174	0.191	0.205	0.176	0.174	0.174	0.179	0.177	0.164	0.176
Duplicates, 5 ppm by weight, humic; 5 ppm by weight fulvic acids													
I/M	0.167	0.160	0.169	0.170	0.184	0.203	0.175	0.173	0.175	0.178	0.170	0.158	0.173
2/M	0.159	0.158	0.174	0.176	0.190	0.201	0.177	0.179	0.172	0.173	0.173	0.160	0.175
Mean	0.163	0.159	0.172	0.173	0.187	0.202	0.176	0.176	0.174	0.176	0.172	0.159	0.174
F ratio	1.24	3.95	1.24	0.90	0.87	5.07	4.21	1.26	5.14	2.04	5.24	2.03	1.03

[a] Critical value of *F* for 3 and 4 degrees of freedom, as in this case, at 5% level is 6.59.
Concentration of priority pollutants 0.16 to 0.20 mg/liter.

All sets contained 0.5% by weight NaCl. Analysis of one of the duplicate preparations of each set was done on one day, the other on the following day by ICP-AES using ultrasonic calibration standards containing only 1% nitric acid. *F* ratios were calculated for each element, and none can be called significantly different at the 5% level of critical values of *F*.

III. CONCLUSIONS

Inductively coupled plasma-atomic emission spectroscopy has already been shown to be a viable technique for providing rapid, precise, and accurate quantitative analysis of environmental samples. Data presented demonstrate that ICP-AES analytical qualities can be extended, through the use of ultrasonic nebulization, to include analyses requiring ultratrace quantitative data such as EPA's Primary Drinking Water Requirements. Because it can be operated at low carrier flows while maintaining large orifice diameters, the ultrasonic system is superior to the pneumatic system when samples containing solids are to be analyzed. Data shown here (Table VII) indicate that a portion of the particulate or adsorbed sample material is transported by the ultrasonic nebulizer to the plasma torch and detected. Using the proposed method, titanium was not detected using a pneumatic system but was found by using an ultrasonic system and injecting the unfiltered sample. Analysis of these unfiltered samples could not be accomplished using a pneumatic nebulizer because of plugging problems.

Priority pollutant metals analysis by ICP-AES using the ultrasonic system was not affected by the presence of organic pollutants (humic acid 9 ppm, fulvic acid 5 ppm) and moderately high salt concentrations (0.5 wt % NaCl), both of which are often found in environmental waters. While sample types reported here were analyzed using ICP-AES and ultrasonic nebulization, no plugged nebulizers were encountered, no interferences due to desolvation were observed, and no new problems with sample memory were observed. Required rinse times between analyses for both ultrasonic and pneumatic systems are dependent upon sample characteristics rather than on the nebulization system and for the sample types discussed here, rinse times were found to be the same for either system. Briefly, the two systems do not change ICP-AES analysis time requirements, but the ultrasonic system will provide more desirable detection limits and is more trouble free when nebulizer plugging is a problem.

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